X-ray Fluorescence Studies of Electrochemical Systems

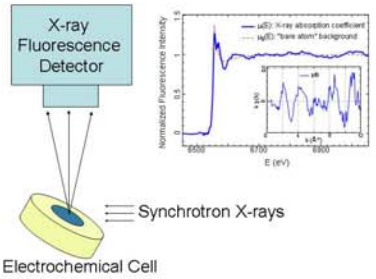
K.-C. Chang[a], A. Menzel[a], V. Komanicky[a], H. You[a],
B. Yildiz[b], D. J. Meyer[c], J. D. Carter[c], J. Inukai[d] and A. Wieckowski[d]
[a]Materials Science, [b]Nuclear Engineering, [c]Chemical Science Divisions, Argonne National Laboratory
[d] Department of Chemistry, University of Illinois at Urbana-Champaign

Motivation

- X-ray Absorption Fine Structure (XAFS) contains information on the adsorbing element's local coordination and its chemical state.
- X-ray measurements are ideal for investigating electrodes in environments similar to actual operating electrochemical devices.

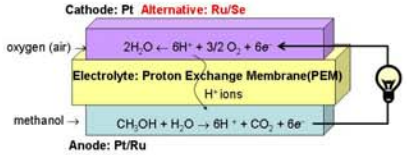
In situ Fluorescence XAFS

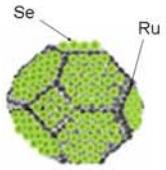
X-ray energy is scanned across the absorption edge of the element of interest. This is done on a sample electrode in an electrochemical cell under potential control.



Ru nanoparticles modified with Se

- **Direct Methanol Fuel Cells (DMFC) have an issue of methanol cross over.**

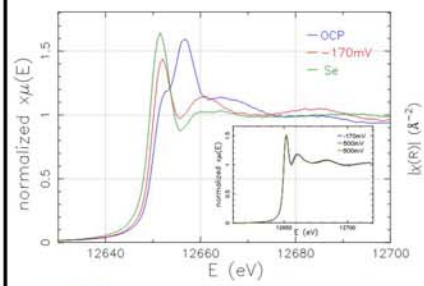




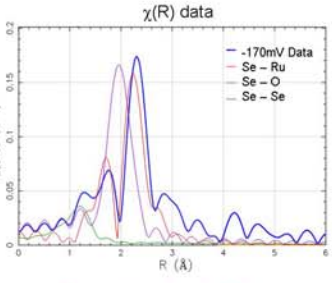
- **Ru/Se is an alternative cathode catalyst which has high catalytic activity for oxygen reduction while being inactive to methanol oxidation.**
- **The stability of new catalyst made by chemically modifying Ru nanoparticles with Se was investigated.**

Ru/Se catalyst was bonded on a carbon pellet with Nafion and immersed in 0.1M H2SO4. XAFS data were taken at different potentials at the Se K edge.

XANES data



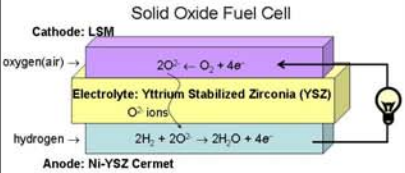
χ(R) data

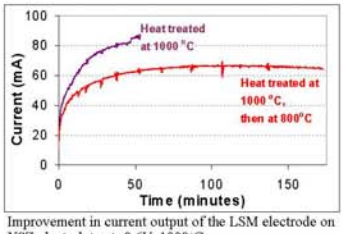


- XANES data at open circuit potential and at -170 mV (vs Ag/AgCl) are markedly different, indicating that Se on the catalyst becomes reduced.
- The XANES does not change up to 0.6V which implies that Se is stable on the catalyst particles in this potential range.
- Predominantly Se-Ru bonds suggesting an electronic effect in operation.

High Temperature Solid Oxide Fuel Cell

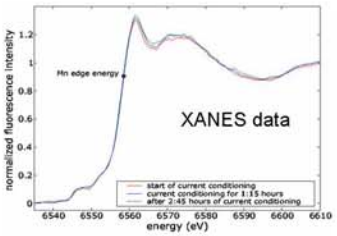
- High temperature Solid Oxide Fuel Cells (SOFC) enable highly efficient conversion of chemical energy into electrical energy. The performance of the $La_{0.8}Sr_{0.2}MnO_3$(LSM) cathode shows long term improvement by *current conditioning*.
- Goal: find the mechanism behind this phenomenon

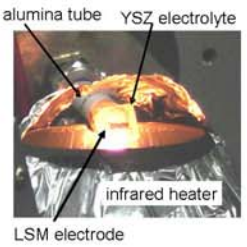




Improvement in current output of the LSM electrode on YSZ electrolyte at -0.6V, 1000°C.

- No change in XANES of the Mn K edge during current conditioning
- Mn oxidation state change is ruled out as a cause of activation
- Structure measurements are in progress.

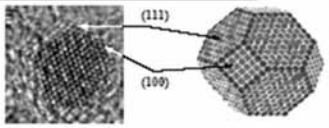


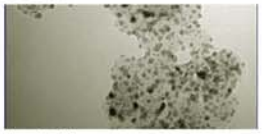


Cell for in situ x-ray investigation of SOFC cathodes under electrochemical control at temperature of up to ~1000°C

CO on Pt nanoparticles

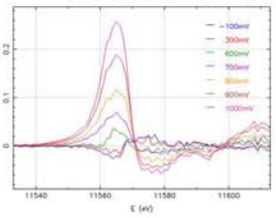
- XAFS is well suited for obtaining fundamental scientific data on real commercial catalysts.
- We have investigated the CO oxidation of Pt catalysts manufactured by E-TEK inc.



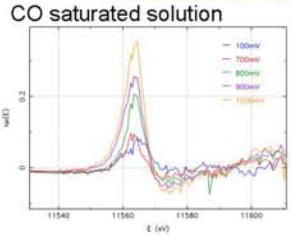


Difference XANES data

Ar saturated solution



CO saturated solution



Our measurements demonstrated the sensitivity of our techniques to the buried interfaces of nanoparticles and their oxidation states. We will study nanoparticle electrocatalysts important to various fuel cells, in situ under respective operating conditions using advanced x-ray fluorescence techniques.

K.C. Chang, A. Menzel, V. Komanicky, J. Inukai, A. Wieckowski, Y. Tolmachev, and H. You, a review chapter to "In-situ Spectroscopic Studies of Adsorption at the Electrode and Electrocatalysis", ed. S. Sun, P.A. Christensen, A. Wieckowski, Elsevier, 2006 in press.

ARGONNE NATIONAL LABORATORY

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